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A DETERMINATION OF THE RATIO (κ) OF THE
SPECIFIC HEATS AT CONSTANT PRESSURE
AND AT CONSTANT VOLUME FOR AIR,
OXYGEN, CARBON-DIOXIDE,
AND HYDROGEN.

BY

O. LUMMER AND E. PRINGSHEIM.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION.
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ADVERTISEMENT.

The present memoir is the result of a series of investigations by Doctors O. Lummer and E. Pringsheim, of Charlottenburg, Germany, aided by a grant from the Hodgkins Fund of the Smithsonian Institution.

After a period of notable advance the kinetic theory of gases seems to have fallen into temporary abeyance, possibly from a fundamentally imperfect understanding of their behavior.

Progress in knowledge of this fundamental nature of gases may reasonably be looked for from interpretative researches on their thermal capacity, and the following paper may be regarded as a step in this direction.

Aside from its exceptional importance in thermodynamics, the specific heat ratio is of interest as affording a clue to the character of the molecule; and Messrs. Lummer and Pringsheim, using a new method, appear for the first time to have reached coincident results on the incoercible gases examined.

In accordance with the rule adopted by the Institution, the work has been referred for examination to a Committee consisting of Professor Doctor Friedr. Kohlrausch, President of the Physikalisch-Technische Reichsanstalt of Berlin, Doctor Carl Barus of Brown University, Providence, R. I., and Professor F. W. Clarke of Washington City; and, having been recommended for publication, the original memoir, submitted to the Institution in German by Doctors Lummer and Pringsheim, is herewith presented, translated into English by Doctor Barus, in the series of Contributions to Knowledge.

S. P. LANGLEY,

SECRETARY.

Smithsonian Institution,

Washington, June, 1898.

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A DETERMINATION OF THE RATIO (κ) OF THE SPECIFIC HEATS AT
CONSTANT PRESSURE AND AT CONSTANT VOLUME FOR AIR,
OXYGEN, CARBON-DIOXIDE, AND HYDROGEN.

BY O. LUMMER AND E. PRINGSHEIM.

INTRODUCTORY.

The experiments detailed in the following pages are based on a method of research,¹ which in all its essential features we had carried through for air as far back as the year 1887. The data obtained in this original test were mutually accordant to within as little as $\frac{1}{4}\%$, but their absolute value was decidedly too small, throughout.

The researches, however, were quite sufficient to convince us that the bolometric method of temperature measurement is well adapted for the *direct* determination of such increments of temperature as are met with in the adiabatic expansion of gases; but that the method, nevertheless, can be expected to lead to trustworthy results only when an extreme of sensitiveness and efficiency has been imparted to the bolometric thermometer. This must therefore be practically instantaneous in its registry (*i. e.*, free from inertia), and the effect of heat conducted either way through the terminals must be eliminated. It is to the latter source of error that we chiefly attribute the discrepancy in our earlier results.

In the meantime bolometric resistances² meeting every requirement had been successfully constructed. Thus it seemed reasonable to assume that in a repetition of the above experiments with the new bolometric material now available, the error due to terminal heat conduction might be reduced in any desirable degree. We were therefore fortunate in being able to repeat our work at the Physikalisch-Technische Reichsanstalt in consequence of a grant from the Hodgkins fund which

¹ *Verhandl. d. Physik. Ges. zu Berlin*, 1887, pp. 136-140.

² O. Lummer and F. Kurlbaum: *Wied. Ann.*, vol. xlv., pp. 204-224, 1892; *Zeitschr. f. Instrumentenkunde*, vol. xii., pp. 81-89, 1892.

was courteously placed at our disposal by the Smithsonian Institution in Washington. It gives us much pleasure again to tender to the Institution our grateful acknowledgments for the favors received.

The results of the present investigation were communicated by permission to the British Association at the Oxford meeting.¹ We purposely withheld the publication of the body of our work, however, inasmuch as we hoped to carry the experiments forward into regions of much higher temperature and to include these results, the preliminary preparations for which had long been completed, in a single memoir. In view of the technical difficulties encountered in the further development of our work, this plan was abandoned. It will take some time before the necessary experience for the construction of high-temperature baths of sufficient constancy is at hand.

1.—THE METHOD IN PRINCIPLE.

The method used for the measurement of the specific-heat ratio of gases depends, in the present as in preceding investigations in the same direction, on the law of *adiabatic* expansion of the gas under treatment. For the case of a *perfect* gas expanding adiabatically from an initial pressure p_1 to a final pressure p_2 , the ratio of absolute temperatures, T_1 and T_2 , corresponding to p_1 and p_2 , may be written ($T_1 > T_2$)

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2} \right)^{\frac{\kappa-1}{\kappa}} \dots \dots \dots (1)$$

where $\kappa = \frac{c_p}{c_v}$ is the ratio of the specific heats at constant pressure and at constant volume. From equation (1) κ is found as

$$\kappa = \frac{\log \frac{p_1}{p_2}}{\log \frac{p_1}{p_2} - \log \frac{T_1}{T_2}} \dots \dots \dots (2)$$

Hence κ may be computed if a perfect gas is permitted to expand adiabatically in such a way that p_1 , p_2 , T_1 , and T_2 are all measurable. For the case of a gas compressed at the temperature T_1 as far as the pressure p_1 , suddenly expanding to atmospheric pressure p_2 , the three quantities p_1 , p_2 , T_1 are found with relative ease. The chief difficulty lies in finding the temperature T_2 , or the final temperature of the gas which has been cooled by sudden expansion from p_1 to p_2 : for the change of temperature from T_1 to T_2 must invariably occur in a very short time if the change of pressure is to be rapid enough to be compatible with the conditions of adiabatic expansion. On the other hand the cooled gas will not remain at the

¹ Report, British Association, Oxford, 1894.

temperature T_2 longer than an excessively brief interval, seeing that heat is continually poured into it from without.

II.—THE METHOD IN PRACTICE.

— *a.* PLAN OF THE EXPERIMENTS.

To hold the charge of gas we made use of a large receiver of spun copper nearly spherical in form and about 90 litres' capacity.

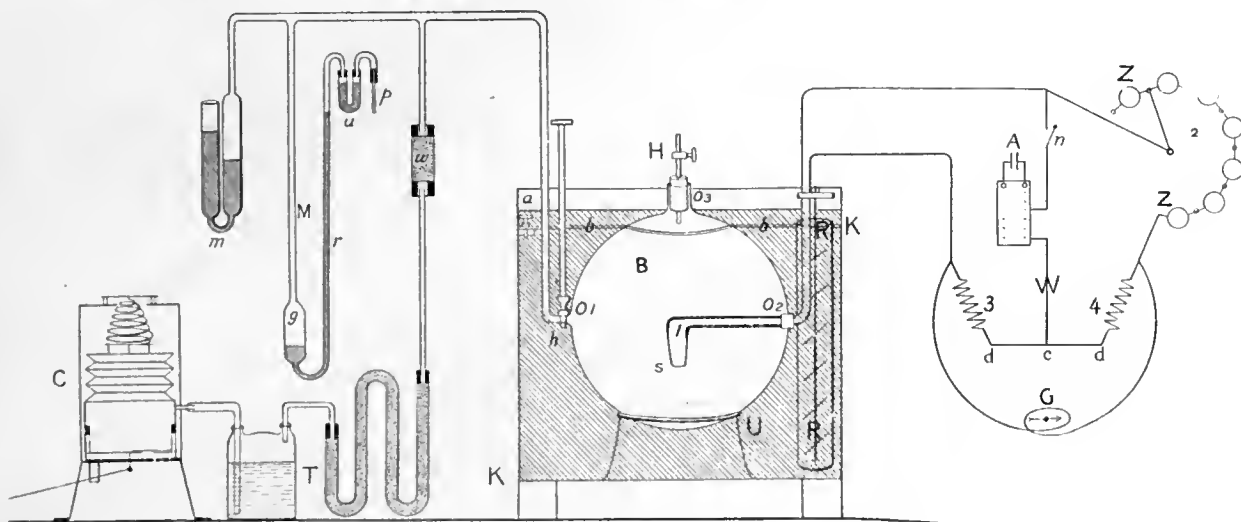


FIGURE 1.

This receiver *B* (fig. 1) contains three tubulated openings, one of which, shown laterally at O_1 , may be closed with a stopcock *h*. This communicates in the manner seen in the figure with the manometers *M* and *m*, the drying apparatus *T*, and the compression pump *C*, by which the gas can be condensed in any necessary amount. If commercial oxygen, hydrogen, or carbon-dioxide is used, the gas may be tapped directly out of the high-pressure cylinders, through the drying train *T* into the receiver. The cock *h* is closed whenever the charge of gas is allowed to expand into the atmosphere.

The second lateral tubulure, O_2 , is adapted to receive the bolometer strip *s*, which represents one branch (1) of the Wheatstone bridge *W*. The other branches (2, 3, 4) consist of suitably chosen resistance standards. For reasons relating to the heat-conduction discrepancy, the form given to the strip of the bolometer is as shown in fig. 2. The strip is cut from a piece of platinum-silver foil, in which the



FIGURE 2.

layer of silver is about ten times as thick as the coextensive platinum layer. In our definitive experiments the thickness of platinum foil used did not exceed

.00006 cm. With the aid of a suitable steel ruler and a thin sharp knife, we were able to cut a strip from the foil which between the rapidly narrowing end flaps *a* and *b* was but .02 cm. in breadth throughout a length of about 10 cm. After the end flaps (each about 4 cm. long and .5 cm. broad) had at their extreme edges been soldered to thick copper terminals, the middle of the strip was dipped in concentrated nitric acid to remove the silver from the platinum film to be used.

The resistance of the platinum bolometer strip etched off for a length of 7 cm. was about 80 ohms, while the resistance of the parts not freed from silver was computed as about .4 ohm, only .03 ohm of which makes up the total resistance of the flaps.

The third opening of the receiver is shown at *O*₃ and used as an avenue of efflux. Its diameter in the clear was 3 cm., and it was closed with a perforated rubber stopper, through which a wide glass stopcock *H* was inserted. Either by suddenly removing the rubber stopper, or in like manner wholly or partially opening the stopcock *H*, we had it in our power to vary the interval of expansion within a wide range.

A large zinc-lined wooden tank *K*, filled with water and surrounding the receiver served the purposes of a water bath. To compensate for the buoyancy of the receiver, sufficient counter pressure was applied through the perforated wooden yoke *b*, which on being forced down by the screw *a* held the receiver firmly down upon the annular tripod *U*. Two stirring appliances *R* were fitted to the diagonally opposite corners of the water bath. These consisted of zinc cylinders, open at both ends and containing an axial propeller-like rotating screw. Actuated by a small electromotor these screws were efficient in producing a flow of water in the zinc cylinders either from below upwards or in the reverse direction at pleasure. If the propelling screws within the cylinders rotate in contrary directions, a circulation of water in the bath will ensue from the surface downward near one of the stirrers, thence along the bottom to the opposite stirrer, which carrying the water aloft stimulates the return circulation along the surface. Small floating bodies like strips of paper gave evidence of the rate at which the current was moving.

b. MEASUREMENT OF TEMPERATURE.

To register the temperature of the water bath we used a calibrated thermometer graduated in tenth degrees. This was read off by a microscope of low power, provided with an ocular micrometer. Continually observing this thermometer, and adding small quantities either of cold or hot water according as the thermometer showed a leaning toward higher or lower temperatures, we succeeded in keeping the temperature of the water constant to about a hundredth of a degree,

frequently throughout a whole hour. Aside from this manipulation, the experiments were favorably circumstanced inasmuch as they were made in the subterranean chambers of the Reichsanstalt. On bringing the temperature into coincidence with that of the room, the observed changes would not exceed the mere fraction of a degree for hours.

Accurate measurement of temperature is of extreme importance in its bearing on the present experiments, since an error of but $.02^{\circ}\text{C}$. in the datum for Z , in the case of the pressure values actually employed, will affect the result by about 1%. To facilitate the reading of the $.01^{\circ}\text{C}$. required, all temperatures were so chosen as to make the mercury meniscus of the thermometer coincide very nearly with one of the division marks of the thermometer. After long practice we also learned to keep the temperature constant to $.01^{\circ}\text{C}$. (by adding ice or hot water as occasion required and continued observation of the thermometer), even when the temperature of experiment lay considerably below that of the room. To be sure that the temperature was quite the same at all parts of the water bath, we made a special test in which, while the stirring device was in action, a sensitive thermometer was carried from place to place within the bath. Simultaneously, of course, temperature was kept constant in the lapse of time, at the single place of observation, by the means above set forth. The thermometer probe used in this test was a branch of one of Lummer and Kurlbaum's surface bolometers, carefully jacketed by a tight metallic case and appropriately insulated. The change of internal resistance experienced by this instrument gave us the necessary data for changes of temperature encountered during the excursions from place to place within the bath. These values, given on pages 18, 24, below, showed the variations of temperatures at any one place in the lapse of time, to exceed the differences of temperature for different positions within the bath at any given time, the bath being kept in action in the manner stated. We infer that

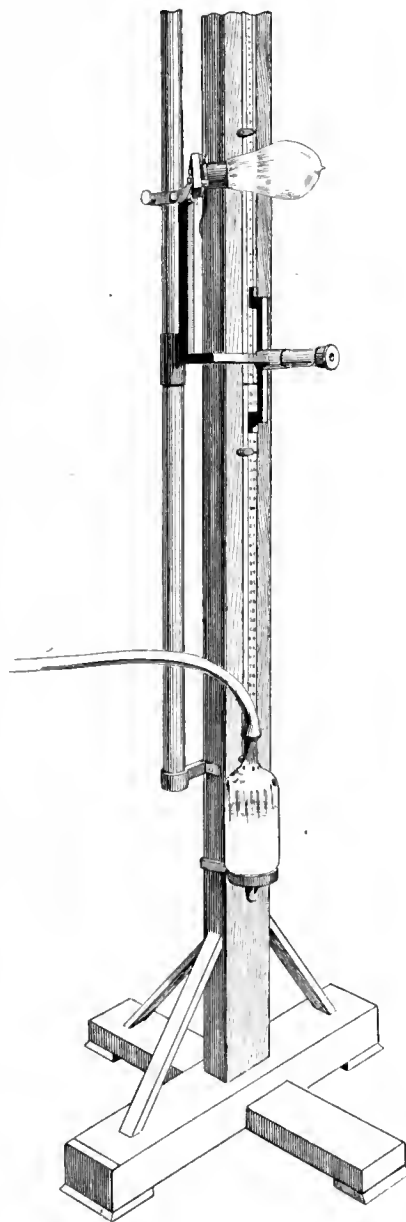


FIGURE 4.

the temperature throughout the whole bath must have been constant to at least .01° C.

C. MEASUREMENT OF PRESSURE.

In like manner the determination of the initial and final pressure of the experiment was pushed forward to a degree of nicety such as would not affect the κ values by more than 1 %. The final pressures were given by the barometer. We availed ourselves of Sprung's barograph as constructed by R. Fuess. The registry of this instrument is certainly correct to fractions of a millimetre, and an error of as much as .2 cm. in the value of the final pressure would have influenced the result by only 1 %. To be quite sure as to the identity of the final pressures with the atmospheric pressures for any given experiment, the efflux tubulure was kept open to the very end of the measurement, *i. e.*, until after the measurement of the temperature T_2 of the cooled gas.

The initial pressures or pressure excesses were registered both by a sulphuric acid manometer and by a mercury manometer of the construction shown in figures 3 and 4. The columns *m* (fig. 1) of the manometer were 4.5 cm. in internal diameter. The pressure tube of the mercury manometer *M* (fig. 1) was 1 cm. in diameter, with a reservoir *g* about 6 cm. in diameter. This instrument was chiefly used to measure pressure excesses during the course of the experiment, while the mercury manometer enabled us to reduce these pressures to their normal value in terms of the barometer. A simple microscope of low power, attached to a suitable slide on the sulphuric-acid manometer stand, enabled us to read off the position of the meniscus in terms of the attached scale. To obviate errors due to parallax, an incandescent mercury lamp was attached to the microscope carriage and moved with it. The scale being attached immediately behind the manometer tube, appeared enlarged when viewed through the part of the tube filled with acid. In this way the position of this meniscus could be read off at this manometer to about .02 cm., corresponding to about .0025 cm. of mercury. For decreasing pressures it was advisable to wait after each change of measurement, until the film of acid adhering to the sides of the tube had reentered the body of the liquid.

The open end of the sulphuric-acid manometer did not directly communicate with the air, but opened into it through a U-tube, *u* (fig. 1), containing calcic chloride and a capillary terminal *p*. In this way difficulties due to absorption of atmospheric moisture by the acid were avoided.

The mercury manometer naturally required much more precise reading than the other. Inasmuch as an error of .3 % in the determination of the pressure excess is equivalent to an error of 1 % in the result, it clearly follows that within this

range of accuracy, pressure excesses of 3.3 cm., 6.6 cm., etc., must be read off within .01 cm., .02 cm., etc., respectively, along the mercury column observed.

To reduce the registry of the sulphuric-acid manometer to that of the mercury manometer we brought to bear on both the same pressure which had been observed during the course of a complete experiment; and for some time after its termination this pressure was maintained at the given value. Not until all pressure variations had fully subsided and permanent constancy of level was assured, did we proceed to the measurement of the equivalent mercury column. The telescope of the cathetometer was then alternately directed to the two menisci of the mercury manometer. In view of the large diameters of the tubes used, the middle parts of the terminal mercury surfaces were appreciably plane. Sharp lines of demarcation being desirable in the field of the cathetometer (preferably separating a dark shadow from a bright background), it was found expedient to illuminate the tubes of the manometer from behind. An incandescent lamp shining through a film of translucent tissue paper was therefore placed at such a level, that no light was reflected from either mercury meniscus into the cathetometer. Lamp and screen were movable up or down, so that the best illumination corresponding to any height of meniscus was attained. It is advisable to place the upper edge of the screen but very little above the mercury meniscus. At the same time the unavoidable specks of dust which float on the mercury surface are of much value in sighting. Our measurement of differences of level was correct to .01 cm. For an initial pressure of 3.3 cm. therefore, the value of κ obtained would not from this cause be discrepant by more than 1 %. A mercury thermometer suspended in the open tube of the mercury manometer showed its temperature. The excellent cathetometer used in these measurements was placed at our disposal by Mr. G. Hansemann, a courtesy for which we take pleasure in expressing our indebtedness.

d. MEASUREMENT OF THE FINAL TEMPERATURE, T_2 .

Two distinct measurements are necessary to complete the determination of T_2 . The decrement of resistance experienced by the bolometer strip while the pressure of the expanding gas falls from p_1 to p_2 is first to be found. Thereafter this electric datum is to be expressed in its equivalent of temperature.

1. Measurement of the initial pressure p_1 , corresponding to the resistance increment w_1, w_2 .

Suppose the initial conditions to be fully established, and let the bolometer strip be at the temperature T_1 of the gas, compressed as far as pressure p_1 . Let

the resistance of the strip be w_1 . Suitably selecting the correlative resistances 2, 3, 4 of the Wheatstone bridge (fig. 1), the sliding contact may be so moved that the galvanometer is without current, indicating the usual balance of resistances. To be in correspondence with the approximate resistance (80 ohms) of the bolometer strip, the branch 2 consisted of a set of standards Z (given in full in fig. 5), the resistance of which could be made very nearly equal to that of the strip. The branches 3 and 4 contained coils suitably wound of standard wire, having about 75 ohms apiece. One end of each of these was connected with the bridge wire d .

The storage cell A , short-circuited through a resistance box, furnished the current. From two points of the box measuring currents of suitable magnitude could thence be tapped into the bridge. Care was taken to keep down the intensity of these currents, in order that appreciable heating of the bolometer strip would not have to be feared. Thus the galvanometer G when in adjustment showed no deflection, either on closing or on opening the circuit at the key n .

When the electrical or thermal condition has thus become stationary and the stopcock O_3 of the receiver is then suddenly opened, the gas will precipitately expand, cooling off both itself and the bolometer, and the galvanometer now shows a definite deflection. It is our problem to find the temperature T_2 of the strip at the instant when the *temperature depression of the gas is a maximum*, by availing ourselves of the electrical registry w_2 . Let us assume in the first place that the temperature of the strip and that of the surrounding gas are at all times identical. Instead of considering the initial pressure p_1 given, to find the resistance decrement w_1-w_2 corresponding to the pressure decrement p_1-p_2 , let us preferably adopt an inverse method in the following way: Start with a given resistance decrement w_1-w_2 ; then by trial and error continually change the initial pressure p_1 until the resistance w_2 of the bolometer strip exactly corresponds to the maximum temperature depression of the gas. No doubt this is a somewhat cumbersome method, but it has the advantage that the galvanometer is used with the needle in the zero position only. It is at least practicable in the definite and final measurements, after the approximate values of the correlated quantities p_1-p_2 and w_1-w_2 are already known.

The approximate values referred to can be found either by computing backwards from known values of κ , or by the following direct procedure. At the gas pressure p_1 and temperature T_1 let the bridge be adjusted. Then let the resistance of the standards Z be reduced from W_1 to any suitable value W_2 . The bridge is thereby thrown out of adjustment and the galvanometer needle will show a deflection. For convenience in designation let the direction of this deflection be called

PLATE I.



FIGURE 3

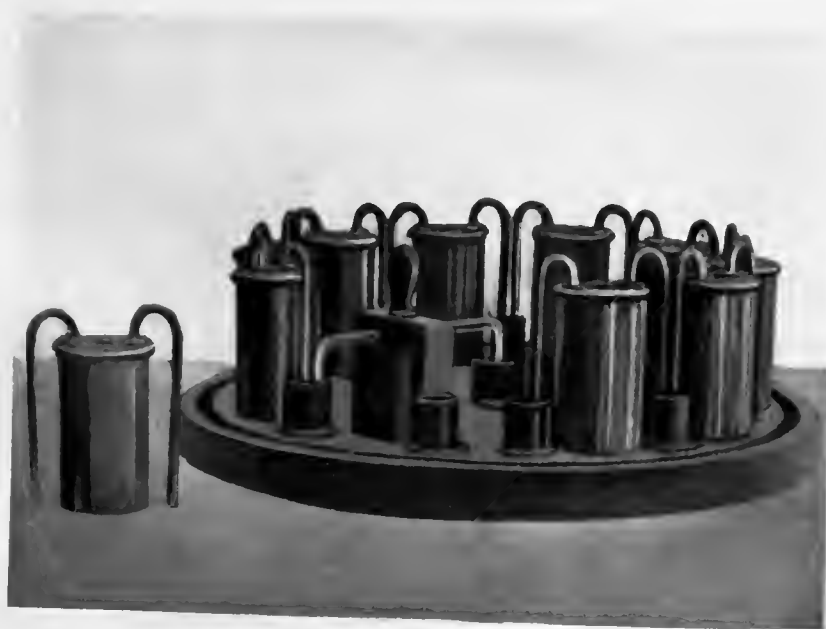


FIGURE 5

positive or negative according as the resistance in Z is larger or smaller than the equilibrium value. When the deflection due to the changed resistance in Z has become permanent, let the receiver be opened and note the effect of expansion on the galvanometer needle. Then according as the arbitrary change of resistance at Z is too large or too small, the needle will move beyond its normal position of equilibrium, or it will stop and return before reaching it from the new position of equilibrium. Owing to the inertia of the needle such results are not very accurate, and they are in large measure dependent on the rate of efflux of the gas. A rather insensitive galvanometer (or one made so by proper shunting) is necessary in these trials because of the relatively great resistance decrements encountered.

If it be granted that the temperature of the gas is always identical with that of the bolometer strip, and that furthermore the maximum of cooling coincides in date with the maximum elongation of the needle, then in addition to furnishing approximate values for w_1-w_2 and p_1-p_2 , the experiments throw light also on the time consumed by the gas in passing to its lowest temperature.

Guided by this introductory work we were able to avail ourselves of the following much more accurate method without unduly sacrificing time. Let the pressure p_1 (known approximately from the preceding experiments) be established, and let the bridge be adjusted for the temperature T_1 . The approximate value w_1-w_2 corresponding to p_1 being given, let the current be broken and the resistance of the standards Z be lowered from W_1 to W_2 , without change in the position of the sliding contact c . While the bridge is thus thrown out of adjustment and the current broken, the gas is allowed to expand, but the current¹ is to be made by closing the key n of the bridge only after the bolometer has reached its minimum resistance.

After some practice it was always possible to so change the initial pressure by small amounts and so vary the estimated period of expansion, that the needle of the galvanometer remained quite at rest² for some time after making the current.

When the correct pressure p_1 has been found, this value may easily be checked, since for initial pressures either slightly less or slightly greater than the true value the galvanometer will show positive or negative deflections, respectively; and thus the datum p_1 can be enclosed between very narrow limits.

¹ It was found preferable to close the current in the battery circuit, not in the galvanometer circuit, in order to obviate errors arising from the presence of thermoelectric currents in the bridge. No temporary thermocurrents arise during the efflux of the gas, as we proved by special efflux experiments made for a circuit open at n . The galvanometer needle remained quite at rest.

² We owe this method ("Einspringmethode") to Dr. Kurlbaum, who took part with us in the original experiments in 1885.

The galvanometer used in these experiments must obviously be provided with a needle which will follow the changes of current in the bridge as quickly as possible. Hence we specially constructed a small galvanometer on the model of Lord Kelvin's instruments. The mirror was suspended from a quartz fibre 5 cm. in length, and carried on its rear face a sufficient number of small lamellar magnets. Deflections were read off with scale and telescope placed at a distance of about 200 cm. from the galvanometer.

To guard against the effect of external magnetic disturbances on the galvanometer, we enclosed it in a double envelope of soft iron. The walls of this chamber were 2-5 cm. in total thickness of solid iron, and were perforated by only a small opening suitable for observing the mirror. Two astasizing magnets were specially provided, one of them placed above the galvanometer on a plate with leveling screws, the other lying on the galvanometer bracket. The latter was additionally useful as a directing magnet. The period of the needle in the final experiments was about 4 seconds, so that a single throw was completed in 2 seconds.

We estimated the period of expansion ("Einspringzeit"), *i. e.*, the time which is to elapse between opening the receiver and closing the galvanometer circuit, by the beats of a metronome, and, after some practice, found it fully vouched for to a fraction of a second. This interval is dependent on the size of the efflux pipe.

2. *Reduction of the resistance increment, w_1-w_2 , to degrees of temperature.*

Having found the resistance w_2 corresponding to the instant of maximum temperature depression, we next proceeded with the measurement of T_1-T_2 , the temperature equivalent of w_1-w_2 . For this purpose, the Wheatstone bridge was first put into balance for the temperature T_1 of the bolometer strip, without, however, compressing the gas. Tests were applied to ascertain whether or not the strip resistance was still w_1 as required. Thereafter the resistance at the standards, Z , was changed to W_2 , and a corresponding depression produced, from without, in the temperature of the water bath (and therefore also of the strip), until the bridge again gave evidence of a balance by reason of absence of current in the galvanometer. This condition was maintained for some time, throughout the whole of which the needle showed no deflection on closing the bridge circuit. The temperature of the bath was now read off and considered identical with the temperature T_2 sought. The datum was corroborated by returning again to the initial temperature T_1 and noting whether w_1 had simultaneously regained its original value.

The advantages which we claim for the present method of reducing w_1-w_2 to T_1-T_2 are not far to seek: In the first place the experiments take but little time,

while in the second almost all the corrections which are usually to be applied in resistance measurement are here insignificant, even when temperature increments of $.01^{\circ}$ C. are in question. For neither w_1 nor w_2 nor their differences need be known in absolute value. The position of the sliding bridge contact, c , alone requires careful attention. This, together with the resistance standards Z in branch 2 of the bridge, including the necessary terminal and connecting wires, must be the same and similarly circumstanced during temperature measurements, as during the actual measurements relative to changes of gas pressure.

Our resistance standards were made of manganine wire. Thick copper terminals and yokes, dipping into large mercury troughs, enabled us to connect the individual units of Z at pleasure. All the connection pieces were stout and of copper wire. Hence changes of temperature in the laboratory were quite without influence on the resistance measurement.

III.—SYSTEMATIC ERRORS.

Before proceeding to a report of the experimental data, we will endeavor to form some estimate as to the effect of systematic errors on the results. The chief assumption in the present and all preceding and similar methods is fundamental: Even supposing the intrinsic equation for the perfect gas to be fully applicable to the actual phenomena, what assurance have we that the expansion obtained is truly *adiabatic*? Rigorously considered, none; for heat will certainly gain access into the interior of the gas. This heat enters partly by conduction or convection; partly by radiation, and its influence on the results will be such as to make the values found for κ smaller than the true values. The influx of heat due to conduction comes partly from the walls of the receiver, partly by direct metallic conduction from the terminals and flaps of the bolometer strip. The former source of discrepancy occurs uniformly in all experiments in which measurements are made relative to an expanding gas. It is just in this respect that the present procedure for κ measurement has distinct advantages over all earlier methods; for these determined T_2 indirectly, by the aid of a special pressure measurement; and therefore the total heat conducted inwards from the walls of the receiver must have entered the results as an error. In our experiments, however, the bolometer strip is suspended in the centre of a large sphere and that part only of this heat can be effective which moves as far as the bolometer through the concentric layers of gas. In virtue of the low order of heat conduction in gases, the time in which heat can reach the centre is so long an interval, in spite of convection, that appreciable rise of temperature at the bolometer cannot occur until the expansion is complete and T_2 fully measured. The superiority of the present method of attack

is evidenced, for instance, by results which show all resistance changes in the bolometer to be independent of the time of efflux, within time limits as broad as 2 to 8 seconds, in the case of air. True, in the best of the earlier experiments, the heat influx from conduction from the walls of the vessel is of serious moment only for the better conducting gases, since the receivers used were all of large capacity. *Röntgen*, however, openly acknowledges that the value of κ for hydrogen found in his experiments must be considerably below its real value. We therefore refer to it as conclusive evidence in favor of our method, that, at variance with the results of all earlier investigators, our method actually gives us a larger κ -value for hydrogen than for air.

Neither can the heat which enters by metallic conduction along the electrical terminals of the bolometer adjustment have produced any serious rise of temperature—certainly not in that part of the gas immediately around the strip. The thin film of pure platinum by which the measurements are virtually made, is free from silver and quite distant from the walls of the receiver. It is, moreover, placed *below* the levels of the terminals, so that true conduction heat only and not convection heat can reach it. For this reason the bolometer temperature remains constant even for several seconds after the completed expansion of air.

Regarding the heat imparted by the bolometer to the gas, the following inferences may be drawn. We have intimated that the measuring current was always reduced to so small a value as not appreciably to change the temperature of the bolometer strip. Hence we may abstract from the Joule heat set free within the film altogether. Similarly the heat which the bolometer strip gives up to the expanding gas is negligibly small; the thermal capacity of the strip, in view of the dimensions stated, is only about .000 007 gram calories. This is about equivalent to the thermal capacity of $\frac{1}{46}$ cm³ of air. Similarly the heat removed from the silver-covered parts of the bolometer is without moment, for these cool very rapidly.

Thus it happens that at least those regions of the gas which immediately surround the etched part of the platinum strip may be regarded as screened from all heat conduction. They therefore expand quite adiabatically.

We have now to consider the question in what degree the temperature T_2 of the gas after expansion, coincides with the actually measured minimum temperature of the bolometer strip. Since the temperature of the bolometer is constant for several seconds during the observation of T_2 , it follows that the bolometer temperature can only differ from that of the gas if there is a permanent flow of heat into the strip. In such a case a stationary distribution of temperature is conceivable, in which the bolometer would impart heat to the gas at the same rate in which it receives it. We can but acknowledge that there must be accession of heat in the

bolometer from the following three sources : (1) as the result of electric current in the strip (this, as we have already seen, being negligible) ; (2) as due to conduction through the terminals ; (3) as due to direct *radiation* impinging upon the strip from the walls of the receiver.

To treat the second case first : the heat received by the strip from the thick terminals may be approximately computed,—at least with reference to the error resulting. We will assume for this purpose that the terminals retain their initial temperature during the whole interval of expansion. Let the bolometer strip be a thin straight conductor, one end of which is kept permanently at the temperature ϑ_0 of the terminals, while the surrounding air is at the temperature ϑ_1 . Let x be the distance of any point of the strip from the terminal end at temperature ϑ_0 , and let ϑ be the temperature at this point at the time t . Hence by Fourier's equation of the temperature distribution in an infinitely long rod subject to radiation

$$\frac{\partial \vartheta}{\partial t} = a^2 \frac{\partial^2 \vartheta}{\partial x^2} - f^2 (\vartheta - \vartheta_1) \dots \dots \dots (3)$$

wherein

$$a^2 = \frac{k}{c \mu}, \text{ and } f^2 = \frac{h u}{c \mu q},$$

and k denotes the coefficient of internal heat conduction.

h , the coefficient of external heat conduction.

c , the specific heat of the strip.

μ , its density.

q , the area of a right section.

u , the circumference of a right section.

But the thickness, d , of the strip is negligibly small as compared with its breadth : therefore

$$\frac{u}{q} = \frac{2}{d}.$$

At the close of the expansion the thermal distribution is stationary along the wire as observation has shown. Hence $\frac{\partial \vartheta}{\partial t} = 0$, and equation (3) becomes

$$a^2 \frac{\partial^2 \vartheta}{\partial x^2} = f^2 (\vartheta - \vartheta_1) \dots \dots \dots (4)$$

If for $x = 0$, the temperature of the strip, we put $\vartheta = \vartheta_0$, and for $x = \infty$, we put $\vartheta = \vartheta_1$, the integral of equation (4) is

$$\vartheta - \vartheta_1 = (\vartheta_0 - \vartheta_1) e^{-x f / a} \dots \dots \dots (5)$$

where $\frac{f}{a} = \sqrt{\frac{h}{k} \cdot \frac{2}{d}}.$

The following values may be assumed for the middle or etched part of the platinum strip :

$$\begin{array}{ll} k = 10, & \mu = 21, \\ h = .003,^1 & d = .0006, \\ c = .03, & \end{array}$$

all quantities being here given in terms of milligrammes, millimetres, and seconds.

Thus f/a is very nearly 1 and we obtain

$$\vartheta - \vartheta_1 = (\vartheta_0 - \vartheta_1) e^{-x} \dots \dots \dots (6)$$

Hence when the gas cools down as far as $\vartheta_0 - \vartheta_1 = 15^\circ \text{C.}$, we find for

$$\begin{array}{ll} x = 0.1 \text{ cm.}, & \vartheta - \vartheta_1 = 6^\circ \text{C.}, \\ x = .5 \text{ cm.} & \vartheta - \vartheta_1 = .1^\circ \text{C.} \end{array}$$

If, therefore, the very thin silver-free platinum film were soldered directly to the stout copper terminals, a fall of temperature would be manifest at the ends of the platinum strip, the influence of which would be far from negligible in its bearing on T_2 .

In view of the interposition of the gradually narrowing or arrow-shaped flap of platinum and silver between the terminals and the effective bolometer strip, the distribution of temperature is materially changed. For the flap in question the constants may be estimated as follows:

$$\begin{array}{l} k = 109, \\ h = .003, \\ c = .06, \\ \mu = 10.5, \\ d = .0066, \end{array}$$

all taken, as before, with reference to milligrammes, millimetres, and seconds, while h is entered unfavorably with a value decidedly large. In this case the quotient f/a is found by computation to be .09, and the temperature distribution for $\vartheta_0 - \vartheta_1 = 15^\circ$ is now such that at a distance of 3 cm., the increment is but 1°C. The effect of using the end flaps of silver is thus a reduction of temperature from the terminals to the strip, fast enough to quite wipe out any serious discrepancy due to unequal temperature in the strips.

In view of the good conduction of electricity by the silver flaps, furthermore, the change of resistance due to change of temperature is equally inappreciable. Thus any marked discrepancy due to conduction of heat along the terminals to the

¹ This number has been obtained for thick rods of iron and German silver. We were obliged to enter it, not having found any special value for platinum. Clearly the quantity h cannot in any real case be a constant. It must increase very rapidly with the decreasing diameter of a given rod. Thus the value above assumed is considerably too small. For very thin rods Cardani finds $h = .06$ (Nuov. Cim., [3], vol. 30, pp. 33-60, 1891). If a larger value for h than the above is put into the equations, the results obtained would be more *favorable* to our argument than those given in the text. Thus if $h = .06$, and $x = 0.1 \text{ cm.}$, $\vartheta - \vartheta_1 = .14^\circ$.

bolometer strip seems to have been effectually excluded in the form of experiment stated.¹

We may also use the Fourier equation to find in what degree the platinum strip coincides with or follows the temperature of the gas. For simplicity we will assume that the gas temperature sinks from its original value (ϑ_0), at a constant rate in the lapse of time. In other words, put

$$\vartheta_1 = \vartheta_0 - b t \dots \dots \dots (7)$$

If now we neglect the heat flux from the ends of the bolometer strip toward the middle,

$$\frac{\partial \vartheta}{\partial x} = 0,$$

and $\vartheta = \vartheta_0$ for $t = 0$. The integral of the general equation (3) thus becomes

$$\vartheta - \vartheta_1 = \frac{b}{f^2} (1 - e^{-f^2 t}) \dots \dots \dots (8)$$

which for $t = \infty$ takes the simpler form

$$\vartheta - \vartheta_1 = \frac{b}{f^2} \dots \dots \dots (9)$$

The difference ($\vartheta - \vartheta_1$) between the temperature (ϑ) of the bolometer strip and the temperature (ϑ_1) of the air has therefore a maximum value of b/f^2 . For the platinum measuring strip (silver removed), the above constants show $f^2 = 15$. Hence the bolometer will coincide in temperature with the air after about 1/15th second. However, since h has been taken very decidedly too small, the real case is correspondingly more favorable. With this deduction our observations agree; for the bolometer reached the stationary state immediately after the noise due to outrush of gas on expansion had subsided.

The last of our sources of error, viz., internal radiation, remains to be discussed. By this agency the bolometer permanently receives heat from the environment, since the walls of the receiver B retain their initial temperature T_1 . But this heat, which is proportional to $T_1 - T_2$, may be computed only if the values of the emission and absorption coefficients of the reciprocating bodies were known. In the absence of satisfactory data for these quantities we made an endeavor to determine the effect of radiation experimentally.

With this end in view, we covered the silver-free part of the bolometer strip, galvanically, with platinum black,² and then repeated the expansion experiments

¹ If with the same constants and in the same manner the fall of temperature be computed for our original device of a bolometric spiral of silver wire, .004 cm. in diameter, the results are such as fully to account for the difference between our earlier values and the present.

² According to the recipe given by Lummer and Kurlbaum, cf. *Verh. der Physik. Gesell.*, Berlin, June 14, 1895.

with the blackened strip so obtained. The high absorptive power of platinum black led us to anticipate an increased temperature difference between the bolometer strip and the air, since this difference, due to the influx of radiant heat from the walls of the receiver, would more appreciably affect the black strip than the bright strip of the usual experiments. Indeed the temperature differences severally encountered should be in the ratio of the absorptions in the two cases. We made a special measurement of the relative absorption of bright platinum and platinum covered in the manner in question, by exposing two surface bolometers, one of which contained the bright platinum foil and the other the platinum-blackened foil, to the radiations of warm water in a copper vessel.¹ These investigations showed that platinum black absorbs the radiations from a copper surface for the temperature interval of 100° C. to 30° C., nearly fifteen times more powerfully than bright platinum. Hence as the change of κ , due to radiation, is now a small quantity, it suffices to deduct the κ value computed by equation (1) for a blackened bolometer strip from the value obtained under otherwise like conditions but with the bright bolometer strip, to divide this difference by 14, and eventually to add the correction so found to all κ values corresponding to uncovered bright platinum foil. This correction is in fact so small that we deemed it sufficient to determine it for air only, and to apply it without further change to the values for the other gases.

IV.—OBSERVATIONS.

a. AIR.

We will premiss the present section by communicating a few tables taken at random from our journal of observations, in order to afford an insight into the general character and the accuracy of our results.

As an example showing the consistency of the results in relation to velocity of efflux, we may cite the pressure measurements for *air* made on the 12th of June, 1893. For an interval of expansion ("Einspringzeit") of 12 seconds for the case of the smallest, and of 2 seconds for the largest efflux opening, the data contained in the two following tables were respectively obtained. The first column in each shows the numbers read off on the scale of the sulphuric-acid manometer² directly. In the second column + shows that the pressure was too large, — that it was too small, while \pm denotes a correct pressure value. The third column contains data for the position of the sliding contact on the Wheatstone bridge, and the fourth

¹ We wish in this place again to thank Mr. Kurlbaum for his active participation in these preliminary experiments.

² The numbers refer to an arbitrary scale, and do not show the height of the column of acid at once. To find the pressure in centimetres of H_2SO_4 , they must be increased by about 26. Cf. data for comparison in table, pages 20, 22.

the temperatures read off on the mercury thermometers. Throughout this temperature measurement the balancing resistance W_1 inserted at Z was

$$70 + 10 + 2^* + 1 + .2 + .2^* + .1 + .5 + 2,$$

of which 2 ohms were inserted before opening the receiver; hence $W_1 - W_2 = 2$ ohms.

The following results were therefore found on July 12, 1893, 12^{sec.} being the period of efflux:

EFFLUX TIME 12^{SEC.}; JUNE 12, 1893.

Manometer.	Pressure.	Bridge.	Temperature. ¹
Mark 25.05	—	598	14.63° C.
25.12	—	594	14.61
25.22	±	595	14.62
25.35	+	596	14.63
25.27	+	597	14.64
25.20	±	597	14.63
25.20	—	598	14.63
25.28	+	598	14.63
25.25	+	597	14.63

These data show that 25.23 cm. is the correct value at the pressure manometer, since 25.20 cm. is obviously low and 25.25 cm. too high.

The data found on the same day for the smallest efflux time of 2 seconds are similarly detailed as follows:

EFFLUX TIME 2^{SEC.}; JUNE 12, 1893.

Manometer.	Pressure.	Bridge.	Temperature.
Mark 25.25	+	597	14.63° C.
25.21	+	597	14.63
25.17	+	597	14.64
25.08	+	597	14.63
24.96	—	597	14.63
25.00	±	596	14.63
25.04	+	596	14.63

To accord with this table, 25.00 must be considered as the pressure value most nearly correct; and indeed the galvanometer needle during this observation remained absolutely at rest for several seconds after expansion. The pressures corresponding to 12^{sec.} and to 2^{sec.} of efflux time, differed on that date only by .23 cm. of sulphuric acid or by .023 cm. of mercury. True, the expansion can no longer be considered adiabatic when the efflux time is as large as 12 seconds, and yet this large variation of the experiment does not change the κ value sought, by more

¹ All the temperatures given are corrected values.

than the equivalent of the pressure difference, or in consideration of the T_1 values applicable, by more than .2 %.

A third complete measurement corresponding to 6^{sec.} of efflux, gave us 25.03 cm. as the correct pressure value at the sulphuric-acid manometer.

The agreement between the reduced values of observations made under like conditions on different days was equally satisfactory.

The temperature measurements corresponding to the experiments to which the above tables apply showed for the resistance W_2 at Z ,

$$W_2 = 70 + 10 + 2^* + 1 + .2 + .2^* + .1 + .5,$$

that there was a balance in the Wheatstone bridge for the temperatures contained in the following table. This table, moreover, gives a good exhibit of the constancy of temperature in the water bath, here definitely below the temperature of the room.

Temperature.	Time.
8.02° C.	11 ^{h.} 46 ^{m.}
8.01	11 55
8.00	12 5
8.00	12 10
8.00	12 15
8.00	12 20
8.00	12 25

Thus the temperature of the air imprisoned at a pressure excess of 25.00 cm., falls during adiabatic expansion from 14.63° C. to exactly 8.00° C.

The pressure comparisons made on June 13 and belonging to the given example are among the following data, where the temperature of the mercury was 18° C. Owing to motion of the mercury columns in the tubes an even number of observations is made for one limb and an uneven number for the other.

Position in the Sulphuric-Acid Manometer.		Mercury Manometer.	
		Upper Limb.	Lower Limb.
1 {	25.15		8.76
		15.32	8.77
	25.15	15.32	8.78
25.15 [cm., H ₂ SO ₄] =		6.55 [cm., Hg.]	
2 {	25.08		8.79
		15.30	8.79
	25.10	15.28	8.79
25.09 [cm., H ₂ SO ₄] =		6.50 [cm., Hg.]	

Hence

Division mark 25.00 H_2SO_4 , = 6.47 cm., Hg, at 18°C .,

" " 25.00 H_2SO_4 , = 6.45 cm., Hg, at 0°C .

Initial temperature $T_1 = 272.4^1 + 14.63 = 287.03$,

Final temperature $T_2 = 272.4 + 8.00 = 280.40$.

The barometer height was found to be 75.97 cm. of Hg.

Thus we find

Initial pressure: $p_1 = 75.97 + 6.45 = 82.42$ cm.,

Final pressure: $p_2 = 75.97$ cm.,

whence

$$\kappa = \frac{\log p_1 - \log p_2}{\log p_1 - \log p_2 - (\log T_1 - \log T_2)} = 1.4021.$$

The following tables are to show in what degree observations made on different days, but under like conditions, agree with each other.

EFFLUX TIME 5^{SEC} ; JUNE 13, 1893, 2nd P.M.

Manometer.	Pressure.	Bridge.	Temperature.
Mark 25.12	+	593	14.63°C .
24.93	—	593	14.64
25.10	+	590	14.63
25.05	+	591	14.63
24.95	—	591	14.63

The barometric height for the day was 76.01 cm., and the value of κ computed for 25.00 at the acid manometer becomes

$$\kappa = 1.4019$$

when the pressure comparison cited above is inserted.

The following table was obtained on the morning of the same day, the barometric height being 76.06 cm. Hg.

EFFLUX TIME 2^{SEC} ; JUNE 13, 1893, 12th M.

Manometer.	Pressure.	Bridge.	Temperature.
Mark 25.02	—	586	14.61°C .
25.17	+	594	14.64
25.12	+	597	14.63
25.07	+	593	14.63
25.10	+	595	14.63

The same pressure, 25.07, at the acid manometer was obtained for an efflux time of 6 seconds, while the needle of the galvanometer remained motionless for 8 seconds. Availing ourselves of the above pressure measurement we thus obtain

$$\kappa = 1.4012.$$

¹ The reasons for preferring -272.4°C . to -273°C . as the position of the absolute zero of temperature will be given on page 25.

Several series of experiments which after a long interval of inactivity were obtained with a new sulphuric-acid manometer and a more accurate cathetometer are now to be given. The first series of experiments was conducted on March 13, 1894, under conditions of low barometric height, 74.42 cm., and for a relatively low temperature, 11.91° C., of the water bath. At this temperature the balancing resistance in the Wheatstone bridge at Z was

$$W_1 = 70 + 10 + 2 + 1 + 2^* + .2,$$

of which $2^* + .2$ ohms were inserted before opening the charged receiver, March 13, 1894.

Manometer.	Pressure.	Bridge.	Temperature.
Mark 13.4	—	589	11.91° C.
15.2	+	589	11.91
13.55	—	589	11.91
14.02	—	589	11.91
14.40	+	589	11.91
14.50	+	589	11.91
14.22	—	589	11.91
14.20	—	589	11.91
14.40	+	589	11.91

The pressure value corresponding to the division 14.21 on the acid manometer was therefore considered correct. Its value was found from the following pressure comparison made when the temperature of the mercury was 20° C.

Sulphuric-Acid Manometer.	Mercury Manometer.	
	Lower Limb.	Upper Limb.
14.30	8.078 cm.	15.20 cm.
	8.080	15.20
	8.076	15.21
	8.075	15.205
	8.085	15.200
14.25	8.088	15.208
	8.088	15.204
	8.085	15.200
14.23	8.081	15.210
	8.099	15.202
	8.099	15.198
	8.101	15.200
	8.095	15.197
14.20	8.096	15.198
	8.104	15.198
	8.099	
14.18		
14.20	8.090	15.190
	8.097	15.190
	8.090	15.202
	8.088	15.190
14.18	8.090	

The mean value of all these data shows that the division mark 14.21 on the acid manometer corresponds to 7.105 cm. of Hg.

The temperature, T_2 , corresponding to the resistance standards at Z ,

$$W_2 = 70 + 10 + 2 + 1,$$

and the position 589 of the sliding contact of the bridge, were deduced from the following data observed on the 10th of February:

Temperature.	Bridge.	Time.
4.31°C.	522	1 ^{h.} 0 ^{m.}
4.31	522	1 5
4.30	522	1 10
4.31	522	1 15
4.31	522	1 ^{h.} 50 ^{m.}
4.31	522	1 55
4.31	522	2 0
4.89	646	2 ^{h.} 10 ^{m.}

From these data we find by interpolation that the temperature 4.64° C corresponds to the position 589 of the sliding contact. Hence the present result is

$$\kappa = 1.3989.$$

Another series of experiments was made on March 16, 1894, when the barometer stood at 75.24 cm. Hg., and the temperature of the water bath was 16.41° C. The resistance standards inserted at Z in the bridge were

$$W_1 = 70 + 10 + 5 + 1 + .5 + .2,$$

$$W_2 = 70 + 10 + 2 + 1.$$

Manometer.	Pressure.	Bridge.	Temperature.
51.15	—	489	16.42° C.
51.45	—	489	16.42
52.25	+	487	16.41
51.55	—	487	16.41
51.88	+	487	16.41
51.70	±	487	16.41
51.62	—	487	16.41

The correct pressure was taken as the equivalent of division mark 51.70. How closely the corresponding mercury pressure has been found will be seen in the following pressure comparisons made on successive days:

MAY 9, 1894.

Sulphuric-Acid Manometer.	Mercury Manometer.	
	Lower Limb.	Upper Limb.
51.75	6.396	18.761
	6.398	18.757
	6.398	18.758
	6.400	18.756
	6.398	18.755
	6.399	18.755

51.70 [cm., H_2SO_4] = 12.358 [cm., Hg].

MAY 25, 1894.—NO. 1.

Sulphuric-Acid Manometer.	Mercury Manometer.	
	Lower Limb.	Upper Limb.
51.75	—	17.185
	4.826	17.185
51.70	4.828	17.187
51.69	4.830	17.186
51.70	4.832	17.187
51.69		

51.71 [cm., H_2SO_4] = 12.357 [cm., Hg].

MAY 25, 1894.—NO. 2.

Sulphuric-Acid Manometer.	Mercury Manometer.	
	Lower Limb.	Upper Limb.
51.70	—	17.186
51.71	4.832	17.186
51.70	4.833	17.185

51.70 [cm., H_2SO_4] = 12.353 [cm., Hg].

The temperature T_2 (4.14°), corresponding to the resistance W_2 , was determined in a way similar to the method given above. These data therefore show

$$\kappa = 1.4012.$$

b. HYDROGEN.

In conclusion we will communicate a similar series of results for hydrogen, selecting data found for three different pressures. The same bolometer strip sub-

served the purposes of measurement as in the preceding experiments. The resistance at Z was at the initial temperature :

$$W_1 = 70 + 10 + .2^* + 5 + .2 + 1 ;$$

and at the final temperature :

$$W_2 = 70 + 10 + .2^* + 2.^* + .5.$$

In the case of hydrogen the period of efflux for corresponding apertures is much smaller than for the other gases.

EFFLUX TIME $1\frac{1}{4}$ SEC.; APRIL 26, 1894.

Manometer.	Pressure.	Bridge.	Temperature.
51.00	+	601	16.01° C.
53.00	+	601	16.01
51.90	± ?	599	15.99
51.40	—	601	16.01
51.60	±	601	16.01
51.85	+	605	16.02
51.55	—	603	16.01
51.65	±	604	16.02

EFFLUX TIME $\frac{1}{4}$ SEC.

Manometer.	Pressure.	Bridge.	Temperature.
51.54	± !	604	16.01
51.20	—	604	16.02
51.65	+	603	16.01

In spite of the shortness of the efflux time ($\frac{1}{4}$ second), the galvanometer needle at the pressure of 51.54 remained quite at rest for *two* (2) seconds. In the following series of experiments all quantities except the position of the sliding contact on the bridge and the initial temperature are exactly the same as in the preceding series; but we operated with a larger efflux opening.

EFFLUX TIME $\frac{1}{4}$ SEC.; APRIL 28, 1894.

Manometer.	Pressure.	Bridge.	Thermometer.
65.00	+	53°	17.31° C.
63.50	—	"	"
64.20	+	"	"
64.00	+	"	"
63.55	—	"	"
63.85	±	"	"
63.65	—	53°	"
63.75	—	53°	"
64.00	+	"	"

In the following experiments for a smaller pressure excess, the change of resistance amounted to 3.1 ohm. The largest efflux opening was made use of.

EFFLUX TIME $\frac{1}{4}$ SEC.; APRIL 28, 1894.

Manometer.	Pressure.	Bridge.	Thermometer.
36.00	+	530	17.31° C.
34.10	—	532	"
35.00	—	"	"
36.00	+	"	"
35.50	!!	"	"
35.70	+	"	"
35.35	—	"	"

The period of quiescence of the galvanometer needle proved at the pressure 35.50 to be quite one second.

We may remark that the observer at the galvanometer was not instructed as to the height of the pressure excess which the second observer produced. The same observer simultaneously kept the temperature of the water bath at the desired value.

C. TEMPERATURE DISTRIBUTION IN THE WATER BATH.

Finally we wish to give a brief summary of the bolometric measurements made relative to the distribution of temperature within the water bath (*cf.* page 5). The mean temperature of the bath in the lapse of time was kept constant in the manner specified above, to the degree given in the first column of the following table. The second column shows the deflection of the galvanometer needle in scale parts, obtained for suitable resistance ratios in the respective branches of the Wheatstone bridge. The third column contains the time of observation. We adduce three series of observations: in the first and third the bolometer was near the surface of the water in the bath, while in the second it was near the bottom.

Temperature.	Deflection.	Time.	Bolometer.
15.70° C.	105.0	1 ^h 17 ^m .	} above
15.70	104.0	1 22	
15.70	104.0	1 27	
15.70	103.0	1 32	
15.70	104.0	1 ^h 37 ^m .	} below
15.70	105.0	1 42	
15.69	103.0	1 47	
15.70	106.5	1 ^h 53 ^m .	} above
15.70	105.5	1 58	

The sensitiveness of the method is particularly seen in the following table of collateral data.

Temperature.	Deflection.	Time.	Bolometer.
15.60° C.	53.0	2 ^h 5 ^m .	} above
15.60	54.0	2 10	
15.60	54.0	2 15	

V.—RESULTS.

Equation (1) which is made the basis of the present experiments applies for perfect gases, the intrinsic equation of which is of the form due to Mariotte and Gay Lussac:

$$pv = RT,$$

where p is the pressure corresponding to the volume v at the absolute temperature T , and R is a constant. For air, oxygen, and hydrogen this equation is admissible, provided the zero point of the absolute scale of temperature be located in conformity with the properties of the gases. This is done if the absolute temperature T is computed from the temperature t in degrees centigrade by the formula

$$T = \frac{1}{\alpha} + t,$$

in which α is the coefficient of expansion of the gas in question. We may remark that the effect of this difference of α for the different gases in question is usually of little significance.

We made the computation in the same way for carbon-dioxide, although the departure from the laws appertaining to perfect gases is appreciable for this body, or at least is larger than for the other gases. The values for α and $\frac{1}{\alpha}$ used in the present paper¹ are as follows:

	α .	$1/\alpha$.
Air0036706	272.4
Oxygen0036743	272.2
Hydrogen0036613	273.1
Carbon-dioxide003699	270.3

a. AIR.

The air was taken directly from the atmosphere in the room and successively passed through concentrated sulphuric acid, a drying tube containing calcic chloride

¹ The values for π communicated at the Oxford meeting of the British Association were found for $1/\alpha = 273$. Hence these results will differ slightly from the present series.

and a wad of absorbent cotton w (fig. 1). Two series of experiments were made: one consisting of 5 determinations in June, 1893; a second series of 6 determinations in February and March, 1894. In the first of these the pressure measurements at the mercury manometer were read off on a cathetometer of only moderate accuracy. The fine cathetometer of Mr. Hansemann was not available until we reached the second series.

In the following tables T_1 and T_2 are the absolute values of the initial and final temperatures, p_1 and p_2 the corresponding pressures of the gas before and after expansion, in cm. of mercury. κ denotes the ratio of the two specific heats, and D the variation of each value from the mean.

Date.	T_1 .	T_2 .	p_1 .	p_2 .	κ .	D .
6, 6, 93	287.02	280.39	82.85	76.32	1.3980	-.0024
12, 6, 93	287.03	280.40	82.42	75.97	1.4021	+.0017
13, 6, 93	287.03	280.40	82.53	76.06	1.4012	+.0008
13, 6, 93	287.03	280.41	82.46	76.01	1.4019	+.0015
16, 6, 93	288.91	276.66	88.69	76.19	1.3988	-.0016

Mean : $\kappa = 1.4004$.

Date.	T_1 .	T_2 .	p_1 .	p_2 .	κ .	D .
9, 2, 94	284.01	276.72	82.28	75.12	1.3996	-.0008
12, 2, 94	289.71	276.46	87.309	74.15	1.4016	+.0012
16, 2, 94	289.63	284.64	81.583	76.78	1.4009	+.0005
16, 2, 94	289.63	279.72	86.753	76.80	1.4000	-.0004
13, 3, 94	284.31	277.04	81.50	74.42	1.3989	-.0015
16, 3, 94	288.81	276.54	87.554	75.24	1.4012	+.0008

Mean : $\kappa = 1.4004$.

The mean values of κ of both series happen exactly to coincide.

The mean value (κ) for data obtained with a platinum-blackened bolometer strip was

$$\kappa = 1.3703.$$

Hence the correction for the radiation discrepancy is

$$\frac{1.4004 - 1.3703}{14} = .0021.$$

The final result for air is therefore

$$\kappa = 1.4025.$$

b. OXYGEN.

Commercial oxygen obtained from Dr. Elkan in Berlin was used. The method of experiment did not differ from that detailed for air. The results are as follows:

Date.	T_1 .	T_2 .	p_1 .	p_2 .	κ .	D .
12, 4, 94	288.71	275.46	89.462	75.80	1.3952	— .0004
12, 4, 94	288.71	282.07	82.291	75.80	1.3948	— .0008
13, 4, 94	289.21	275.61	89.713	75.71	1.3963	+ .0007
13, 4, 94	289.21	279.25	85.694	75.75	1.3969	+ .0013
13, 4, 94	284.71	275.76	84.793	75.75	1.3950	— .0006

Mean $\kappa = 1.3956$.

Correction for radiation + .0021.

Final value (corrected), $\kappa = 1.3977$.

c. CARBON-DIOXIDE.

The gas was obtained from a cylinder of commercial, liquid carbon-dioxide. Hence it was passed through the drying train into the copper receiver for experiment.

Date.	T_1 .	T_2 .	p_1 .	p_2 .	κ .	D .
19, 4, 94	288.01	277.08	89.477	75.54	1.2961	— .0013
19, 4, 94	288.01	280.36	84.998	75.56	1.2965	— .0009
19, 4, 94	280.71	277.41	79.677	75.68	1.2987	+ .0013
19, 4, 94	280.71	274.11	83.986	75.72	1.2983	— .0009

Mean $\kappa = 1.2974$.

Correction for radiation + .0021.

Final value (corrected), $\kappa = 1.2995$.

d. HYDROGEN.

Commercial hydrogen obtained from Dr. Elkan in Berlin was passed through a solution of permanganate of potash and thereafter treated in the manner specified for air.

Date.	T_1 .	T_2 .	p_1 .	p_2 .	κ .	D .
24, 4, 94	285.32	276.35	84.617	75.75	1.4064	+ .0001
26, 4, 94	289.02	276.72	87.930	75.64	1.4062	— .0001
28, 4, 94	290.32	276.47	89.463	75.46	1.4056	— .0007
28, 4, 94	290.32	279.99	85.527	75.46	1.4070	+ .0007

Mean $\kappa = 1.4063$.

Correction for radiation + .0021.

Final value (corrected), $\kappa = 1.4084$.

CONCLUSION.

We have already intimated that the values for κ obtained with the new bolometer would be *larger* than the corresponding data obtained in 1887 by the use of a silver wire .004 cm. thick for bolometric purposes. This anticipation has been quite borne out by the experiments, showing that the discrepancy due to heat conducted inward from the terminals had seriously affected our earlier results.

A summary of the different experiments made for evaluating κ is given by A. Winkelmann in his *Handbuch der Physik*, 1895, vol. ii., pp. 381, 382, covering the ground up to 1895. Furthermore, the *Journal de Physique*, 1895 (3), vol. iv., pp. 463-465, contains an historical and critical review¹ of the subject as to methods and observations, by M. G. Manoevriér. We do not therefore think it advisable to reproduce these bibliographies here, in which, to our knowledge, only the experiments of J. Webster Low² seem to have been overlooked. On the other hand, a comparison of our results with those of earlier observers in the form of a table such as is given at the end of this paper, will conduce to an intelligent survey of the present aspect of the subject. All correlative results were obtained by methods different from ours.

The researches of Röntgen and of Paquet are based on the well-known method of Clément and Desormes.

The values of Kayser, Wüllner, and J. Webster Low are computed from data for the velocity of sound. The first two of these observers made use of Kundt's method, while Low reached his results through the interferential method for the velocity of sound waves devised by Quincke. Manoevriér's method is the following: A given mass of gas is compressed *adiabatically*, and the increase of pressure produced determined. The change of pressure due to an equal but *isothermal* change of volume is easily computed from known laws. If both volume decrements be small, the ratio of the pressure increments is very nearly equal to the ratio of the specific heats. Hence κ may be found from the data for the adiabatic volume reduction.

All data given in the following table refer to ordinary atmospheric temperatures.

¹ In this review, as well as in another paper (*Journal de Phys.*, 1895 (3), vol. iv. pp. 368-373), M. Manoevriér devotes some space to our work of 1887 and to the results of the present investigation, as far as they were given in the brief summary contained in the Reports of the Oxford meeting of the British Association. We consider a direct reply superfluous, for the points raised by M. Manoevriér are all touched upon in the present extended publication in so far as they are matter-of-fact and not merely controversial.

² J. Webster Low, *Wied. Ann.*, vol. lii., pp. 641-664, 1894.

TABLE OF COMPARATIVE VALUES OF κ .

Observer.	Air.	Oxygen.	Carbon-Dioxide.	Hydrogen.
Röntgen, 1873.....	1.4053	—	1.3052	1.3852
Kayser, 1877.....	1.4106	—	—	—
Wüllner, 1878.....	1.405	—	1.3054	—
Paquet, 1885.....	1.4038	—	—	—
J. Webster Low, 1894.....	1.3968	—	1.291	—
Lummer and Pringsheim, 1894...	1.4025	1.3977	1.2995	1.4084
Manoevriev, 1895.....	1.3925	—	1.298	1.384

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